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## PATENT SPECIFICATION



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**510,053**

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### COMPLETE SPECIFICATION

#### Process for the Crystallisation of Alkaline Earth Metal Nitrates

We, AZOGENO SOCIETE ANONIMA, a joint-stock Company, incorporated under the laws of Italy, of 4, Piazza Campetto, Genoa, Italy, and CARLO TONIOLO, an Italian Subject, of the said Company's address, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for the crystallisation of alkaline earth metal nitrates and more particularly of calcium and magnesium nitrates or of mixtures thereof and to the products thus obtained.

It is known that the nitrates of the alkaline earths and particularly calcium nitrate present difficulties in their crystallisation and solidification. Thus when the solutions of such salts are concentrated beyond the point of saturation, the salt does not readily crystallise out, but such solutions often maintain the salt in dissolved form for a long time in a liquid syrupy condition; if the nitrate is melted in its own water of crystallisation and cooled to below its normal solidification temperature, it often remains in a liquid viscous condition for a long time.

On the other hand, it is known that technical nitrate of lime is generally deliquescent. This inconvenience has been overcome by mixing the solid nitrate of lime with variable amounts of salts of ammonia or derivatives thereof, or basic salts. Thus according to British Patent No. 5586 of 1910, a non-deliquescent calcium nitrate fertilizer is obtained by mixing the solid nitrate of lime with ammonium salts and particularly with ammonium sulphate. According to another British Patent No. 180,180, technical nitrate of lime is rendered non-deliquescent by mixing it in the solid state with small amounts of basic salts or of ammonium salts. The patentee justifies this addition because, according to his observations, the deliquescence of the nitrate of lime is due to the presence of traces of free nitric acid, which can be neutralised by the aforesaid additions.

Further it is also known that the

crystallisation of the nitrates of the alkaline earths and especially of nitrate of lime, may be promoted by disturbing the unstable equilibria of the super-saturated solutions by the addition of an ammonium salt, for example ammonium nitrate, or other ammonium salts capable of producing ammonium nitrate by double decomposition. In fact, if the molten nitrate of lime containing even relatively small amounts of ammonium salt is sprayed into the air in the form of very small drops, it becomes crystallised and solidifies during the very short time required for its fall. By this process, which is described and claimed in British Patent No. 249,370, a characteristic product is obtained consisting of nitrate of lime in the form of globular grains containing, in molecular distribution, salts or compounds of the ammonia in an amount of not over 10%.

In French Patent No. 764,440 a process for crystallisation of alkaline earth nitrates, particularly calcium and magnesium nitrates is described wherein a supersaturated solution or supercooled melt thereof is sprinkled or sprayed into small drops which are allowed to fall on to a layer of the same salts, already solid and crystallised, but in a finely divided state; whereas in the process for crystallisation of alkaline earth nitrates particularly calcium and magnesium nitrates according to the present invention a supersaturated solution or supercooled melt thereof is sprinkled or sprayed into small drops which are allowed to fall on to a layer of the same salts, already solid and crystallised, but in a powdered or finely divided state, the process being characterised in that the solid salts forming said layer are previously mixed with ammonium nitrate or with other compounds of ammonia in solid form, and in that the mass constituted by said layer together with the nitrate crystallised thereon is continuously stirred so as to maintain the said mass in a loose condition and to obtain a final product consisting of alkaline earth nitrates in granular form containing some ammonia

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compound in non-molecular distribution.

The mixture is effected between the solid pulverulent salts, that are neither in solution, nor in a molten state, and  
5 therefore the distribution is not physically uniform, and by no means molecular, as is the case with the process according to the British Patent No. 249,370, but quite a rough mechanical distribution is  
10 obtained. This latter is however, sufficient for practical purposes.

This bed is suitably stirred or mixed in such a manner that the small drops of the liquid or molten product may be incorporated into the solid and dry mass and  
15 in this manner the condition of unstable equilibrium is disturbed and the crystallisation, i.e. the solidification, of the sprayed or sprinkled product, is promoted.

In order to avoid undesired persistence of the supersaturated or supercooled condition, the quantity of the bed-forming solid and of already cooled salt should be such as not to permit of the whole mass  
20 becoming excessively hot due to the heat developed by the crystallisation or solidification of the nitrate dropped thereon or mixed therewith, as otherwise the whole mass would become soft and pasty instead  
25 of remaining as a loose and granular powder and, in order to attain a continuous production, the bed-forming layer must be regularly mixed thoroughly and replaced from time to time with a new  
30 mass of material adapted to constitute a fresh bed.

The product as obtained is, however, neither in the form of drop-like globules, nor is the ammonium nitrate contained  
40 therein in a molecular distribution; the product resembles more that obtained according to the said British Patent No. 180,180, but its grains are on the average sufficiently regular and it is not deliquescent or hygroscopic and is very suitable for use for all technical purposes, or for use as a fertilizer. The crystallization of such product is very simple and does not require particular care, as the  
50 nitrate being sprayed or sprinkled in the form of very small and numerous drops on the pulverulent bed is spread over a very large area adapted to give off the heat of solidification to the surrounding air;  
55 moreover a part of the heat which would remain in the solidified product is distributed in its turn throughout the bed-forming dry granular or pulverulent material, thus permitting each crystallising operation to be protracted.

We are aware that it is well known that the condition of unstable equilibrium due to supersaturation can be disturbed by the addition of crystals of the same salt;  
65 if however, to a molten mass weighing

some hundred weights or some tons and kept, for example, in a container (tub, vat or rotating cylinder) some solid nitrate of lime were added, the solidification would not take place easily due to  
70 the fact that the cooling of this mass would take place from a relatively small surface area and the mass would warm up (due to the heat evolved in solidification) and would thus remain in its molten and  
75 pasty state. And even if cooling means were resorted to (such as cooling coils or water-sprayed surfaces, which might well be rendered inefficient, more or less rapidly due to the formation of incrustations of solid salts), the whole mass at the end would clog into a solid or pasty block, which would be very difficult to extract and crush. On the contrary by  
80 proceeding in the manner described hereinbefore, a product is obtained which always keeps its loose, granular or pulverulent form and never clogs into blocks or a pasty mass and therefore does not require a subsequent crushing.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for crystallisation of alkaline earth nitrates, particularly calcium and magnesium nitrates according to which a supersaturated solution or supercooled melt thereof is sprinkled or  
95 sprayed into small drops which are allowed to fall on to a layer of the same salts, already solid and crystallised, but in a powdered or finely divided state, characterised in that the solid salts forming said layer are previously mixed  
100 with ammonium nitrate or with other compounds of ammonia in solid form, and in that the mass constituted by said layer together with the nitrate crystallised thereon is continuously stirred so as to maintain the said mass in a loose condition and to obtain a final product consisting of alkaline earth nitrates in granular form containing some ammonia  
105 compound in non-molecular distribution.

2. A process as claimed in claim 1, in which the crystallisation bed-forming layer that is constituted by the rough mixture of alkaline earth nitrate and  
120 ammonium salt is distributed upon a large surface area which is exposed to the air in order to facilitate the dispersion of the heat evolved on solidification.

3. A process as claimed in claim 1 or 125 2, in which the pulverulent or granular layer constituted by the original bed and by the nitrate of the alkaline earth crystallised thereupon or therein is so abundant and is so regularly substituted  
130

by a fresh layer as to provide that its temperature does not rise sufficiently high (due to the evolution of heat of crystallisation) as to promote a partial melting or a softening and consequently a clogging of the crystallised nitrates.

4. The granular or pulverulent product constituted by alkali-earth nitrates containing in a non-molecular distribution ammonium salts or compounds whenever

obtained by the crystallisation process substantially as described and claimed.

5. The process for crystallisation of alkaline earth metal nitrates, substantially as herein described.

15

Dated this 3rd day of August, 1938.

W. P. THOMPSON & CO.,  
12, Church Street, Liverpool, 1,  
Chartered Patent Agents.

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